

PREPARATION OF NANOFILTRATION HOLLOW FIBER MEMBRANE FOR ACETIC ACID REMOVAL FROM SYNTHETIC HYDROLYSATE

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ABSTRACT

Nanofiltration has a pore size range of 0.001-0.01 μ m. NF membranes can filter particles up to and including some salts, synthetic dyes and sugars, however it is unable to remove most aqueous salts and metallic ions, as such, NF is generally confined to specialist uses. Nanofiltration (NF) is a promising membrane separation technology due to its low energy consumption and unique separation properties. The main objective of this research is to produce, characterize and evaluate performance of PES NF hollow fiber membrane for acetic acid removal from biomass hydrolyzate solution. An asymmetric PES hollow fiber membrane was fabricated using a dry/wet spinning process with forced convection in the dry gap. The PES concentration be fix at 20wt%, but the value of additive (PVP) is increase from 1wt% and 9wt.% and the rest is the value for NMP which act as solvent. The membranes were then analyzed by using scanning electron microscope (SEM) and high performance liquid chromatography (HPLC). Increase the concentration of PVP resulting decreased the rejection of the component it will increase the number of pore at the membrane and resulting in permeability of the membrane which increase of concentration of PVP will increase the permeability of the membrane. The increasing of additive concentration tends to increase the salt permeability while reducing the effective membranes thickness. In this case, the thickness of the effective membrane layer (dense layer) is very important and well known as one of the determining factors influencing the membranes separation ability.

Keywords: Nanofiltration membrane, Hollow fiber Module, Biomass

ABSTRAK

Nanofiltration mempunyai pelbagai saiz liang 0.001-0.01 μ m. Membran NF boleh menapis zarah sehingga dan termasuk beberapa garam, mati sintetik dan gula, bagaimanapun ia tidak dapat menghapuskan garam akueus dan ion logam, oleh itu, NF biasanya terhad kepada pakar menggunakan. Nanofiltration (NF) adalah membran menjanjikan pemisahan teknologi kerana penggunaan tenaga yang rendah dan sifat pemisahan yang unik. Objektif utama kajian ini adalah untuk menghasilkan, mencirikan dan menilai prestasi PES NF serat berongga membran untuk penyingkiran asid asetik dari penyelesaian Hidrolisat biomassa. Satu PES simetri membran gentian geronggang telah dibikin menggunakan proses berputar kering / basah dengan olakan paksa dalam jurang kering. PSB kepekatan akan menetapkan di 20wt%, tetapi nilai tambahan (PVP) adalah peningkatan daripada 1wt% dan 9wt.% Dan selebihnya adalah nilai untuk NMP yang bertindak sebagai pelarut. Membran kemudiannya dianalisis dengan menggunakan mikroskop imbasan elektron (SEM) dan kromatografi cecair prestasi tinggi (HPLC). Meningkatkan kepekatan PVP Hasilnya, Syarikat menurun penolakan komponen ia akan meningkatkan bilangan liang pada membran dan menyebabkan kebolehtelapan membran mana kenaikan penumpuan PVP akan meningkatkan kebolehtelapan membran. Peningkatan kepekatan tambahan cenderung meningkat kebolehtelapan garam di samping mengurangkan ketebalan membran yang berkesan. Dalam kes ini, ketebalan lapisan membran yang berkesan (lapisan padat) adalah sangat penting dan terkenal sebagai salah satu faktor yang menentukan mempengaruhi keupayaan membran pemisahan.

Keywords: membran Nanofiltration, Modul serat Hollow, Biomassa

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LIST OF ABBREVIATIONS

A_0	constant of eq.(3.6)
A_s	constant of eq.(3.6)
a	interfacial area per unit volume
$a(L_i)$	breakage kernel
$b(k, L_i)$	daughter bubble distribution function
B	nucleation kernel
C	impeller off-bottom clearance
C_o^*	oxygen solubility in water
C_D	drag coefficient
v_g	superficial gas velocity
VVM	volume per unit volume
w	weight
W	impeller blade width
Y_v	turbulent destruction term for Spalart-Almaras model

Greek

ν_l	kinematic viscosity
θ_{ie}	collision rate of bubbles with turbulent eddies
κ_i	break-up efficiency
$\Lambda(L_i, L_j)$	bubble collision efficiency

Subscripts

b	bubble
g	gas
l	liquid
eff	effective

LIST OF ABBREVIATIONS

CARPT	Computer-automated radioactive particle tracking
CFD	Computational fluid dynamics
CSP	Capillary suction probe
CT	Computer tomography
DAE	Differential algebraic equation
DES	Detached eddy simulation
DI	Digital imaging
EIT	Electric impedance tomography
ERT	Electric resistance tomography
FFT	Fast Fourier transform
GRT	Gamma ray tomography
IZ	Ishii-Zuber drag model
LDA	Laser doppler anemometry
LES	Large eddy simulation
LIF	Laser image fluorescence
MOC	Method of classes
MOCh	Method of characteristic
MOM	Method of moment
MRF	Multiple reference frame
PD	Product difference
PBE	Population balance equation
PBM	Population balance modelling
PDA	Phase doppler anemometer
PIV	Particle image velocimetry
PLIF	Planar laser induced fluorescence
QMOM	Quadrature method of moment
RDT	Rushron turbine
RANS	Reynolds averaged Navier-Stokes
RNG	Renormalised k - ϵ
RSM	Reynolds stress model
SA	Spalart-Allmaras model
SGS	sub-grid scale
SMM	Sliding mesh method
SN	Schiller-Naumann drag model
SST	Shear stress transport model

1 INTRODUCTION

1.1 Research Background

Lignocellulosic materials such as agricultural, hardwood and softwood residues that produced bioethanol is a promising alternative energy because lignocellulosic materials do not compete with food crops. In a typical bioconversion process to produce “second generation” bioethanol, the hemicellulose is converted to pentose (predominately xylose) by hydrolysis pre-treatments, while the cellulose is converted to hexose (predominately glucose) by enzymatic hydrolysis. After hydrolysis process, these sugars can be fermented and converted to ethanol (Chen et al., 2011)

However, the by-products such as furans, carboxylic acid and phenolic substances, were also generated in the hydrolysis process, which can significantly suppress fermentative organisms and decrease the ethanol yield and productivity. Acetic acid, one of the inhibitors, which was studied in detail due to its highest content in hydrolyzates, is generated by the hydrolysis of the acetyl group on hemicellulose and is commonly observed along with the release of xylose (Mussatto and Robert, 2004). With the presence of acetic acid in high concentration, the growth of fermentation microorganisms and the production of ethanol are strongly affected (Palmqvist and Hahn-Hagerdal B., 2000)

There are several methods to remove acetic acid including dehydration of acetic acid, filtration by membrane and so on. Nevertheless, the application of membrane separation in bio-energy studies, especially for acetic acid removal, is still in the early stages. Pressure-driven membrane processes have drawn great attention in the industry for their unique ability to separate and purify products from process streams including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Applications of NF to the separation, purification and concentration of products from streams have been emerging in various fields, including fermentation product separation, sugar fractionation and sugar concentration (Weng, 2009)

By using nanofiltration membrane, the observed retention of xylose and acetic acid varied from 28% to 81% and -6.8% to 90%, respectively, depending on the solution pH and the applied pressure. The maximum separation factor was 5.4 when the system was operated at pH 2.9 and 24.5 bar. In addition, negative retention of acetic acid was observed only in the presence of xylose. The results suggested that intermolecular interactions play an important role in the separation of xylose and acetic acid (Weng, 2009).

The high demands of sustainable alternative transportation fuels are of interest as second-generation biofuels. One type biofuel is ethanol produced from non-food biomass. It is necessary to increase the ethanol concentration of the product after fermentation to decrease the energy required for the final separation process and to commercialize lignocellulosic ethanol technology. In order to increase the yield of ethanol, acetic acid should be extracted from the enzymatic hydrolyzates because the present of acetic acid limited the production of ethanol. Concentrating enzymatic hydrolyzates which are glucose and xylose using membrane separation process, nanofiltration, with molecular weight cut offs between ultrafiltration and reverse osmosis, is attractive because nanofiltration is a widely used technique in biorefineries due to its low energy consumption and unique separation properties. Membrane is very important part to remove the acetic acid and increase the concentration of glucose and xylose.

Membrane filtration is an efficient, cost-competitive and promising separation method during industrial production process (Pinelo et al., 2009). Applications of membrane technology for, sugar concentration, sugar fractionation, and inhibitor separation from lignocellulose hydrolyzates were studied in recent years. Murthy et al. reported the concentration of xylose reaction liquor can be effectively accomplished by nanofiltration, while Sjöman et al. found that the xylose purification from hemicellulose hydrolyzates could be enhanced by nanofiltration. As the inhibitor with the highest content in hydrolyzates, acetic acid was firstly separated by Han and Cheryan from an acetic acid-glucose model solution by using NF and RO membranes, and acetate rejection of 40% and glucose rejection of 99% were obtained, respectively. Sagehashi et al. employed RO membranes to separate phenols and furfural from the aqueous solution derived from the superheated steam pyrolysis of biomass, and the solution was

concentrated effectively by reverse osmosis separation. Several researchers also reported the separation of carboxylic acids or furans from sugars in dilute-acid hydrolyzates or fast pyrolysis bio-oils by using NF or RO membranes (Qi et al., 2011; Teella et al., 2011; Weng et al., 2009, 2010).

Applications of NF to the separation, purification and concentration of products from streams have been emerging in various fields, such as fermentation product separation (Han I. S, 1995) sugar fractionation (Sjoman E. , 2007) and sugar concentration (Murthy G.S., 2005) In general, NF can distinguish molecules via sieving effect as well as by charge effect. The retention of uncharged molecules by NF will be determined mainly by sieving effects. Molecules with a molecular weight larger than that of the sieving characteristics or exclusion properties of the NF membrane would be rejected.

The separation of multi-valent ions by NF is high due to the Donnan effect. Han and Cheryan were the first to study the separation of sugar from acetic acid. They found the pH is a major factor influencing the separation of acetic acid from glucose. More recently, Sjoman et al. studied the separation of xylose from glucose via commercially available in NF membranes. Murthy et al. reported that concentration of xylose by NF from 2% to 10% (w/v) was successful separated in a pilot plant. In addition, they found the operational costs for xylose concentration by NF were one-fourth that of a conventional evaporation process. Although solution pH is an important factor governing NF performance, the effect of solution pH on the separation performance was not explored in their pilot plant study. To the best of my knowledge, there were only a few investigations on NF separation of acetic acid from monosaccharide except for some studies on downstream processing of acetate by NF after glucose fermentation. Furthermore, there is limited information on the purification of xylose for bioethanol production.

In this study, acetic acid was separated using nanofiltration hollow fibre membrane from xylose and glucose by using different concentration of NMP. Constant pressure was apply while separation to investigate the result of separation of acetic acid from xylose and glucose. From the literatures, NF was concluded as the standard membrane process for acetic acid separation from sugars, due to the negative retention

of acetic acid. Zhou et al., have mentioned the membrane performance of NF and RO membrane for acetic acid separation from monosaccharaides was compared in a comprehensive manner.

1.2 Objective of the Research

The main objective of this research is to produce, characterize and evaluate performance of Polyethersulfone (PES) NF hollow fiber membrane for acetic acid removal from synthetic biomass hydrolysate solution.

1.3 Scope of the Research

In order to fulfill the research objective, the following scopes has been outlined.

- i. To produce two different composition of NF hollow fiber membrane A (20 wt% PES, 1wt% PVP, and 79 wt% NMP) and B (20 wt% PES, 9wt% PVP, and 71 wt% NMP)
- ii. To characterize and evaluate the performance of PES NF hollow fiber membrane using pure solution (xylose, glucose and acetic acid) and synthetic hydrolyzate solution (i.e. mixture of xylose, glucose and acetic acid)

2 LITERATURE REVIEW

2.1 Biomass

Biomass simply define as all plant material, or vegetation, raw or processed, wild or cultivated. Examples of this energy source include fast growing trees and grasses, agricultural residues like used vegetable oils, wheat straw, or corn, yard clippings , wood waste like paper trash, sawdust, or wood chips, and methane that is captured from landfills, livestock, and municipal waste water treatment. Essentially, biomass is stored solar energy that human can convert to electricity, fuel, and heat. The energy from the sun is stored in the chemical bonds of the plant material through photosynthesis. Typically biomass energy comes from three sources for example agricultural crop residues, municipal and industrial waste, and energy plantations. In addition, crops such as corn, sugar beets, grains, and kelp can be grown specifically for energy generation. Table below shows the properties xylose, glucose and acetic acid.

2.2 Biomass Processing

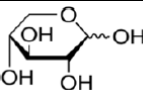
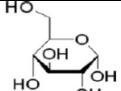
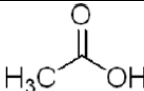
Biomass goes through a size-reduction step to make it easier to handle and to make the ethanol production process more efficient. Figure 2.1 shows the biomass process. For example, agricultural residues go through a grinding process and wood goes through a chipping process to achieve a uniform particle size. Biomass is then being treated. In this step, the hemicellulose fraction of the biomass is broken down into simple sugars. A chemical reaction called hydrolysis occurs when dilute sulphuric acid is mixed with the biomass feedstock. In this hydrolysis reaction, the complex chains of sugars that make up the hemicellulose are broken, releasing simple sugars. The complex hemicellulose sugars are converted to a mix of soluble five-carbon sugars, xylose and arabinose, and soluble six-carbon sugars, mannose and galactose. Table 2.1 show the properties of xylose, glucose and acetic acid. Acetic acid, one of the inhibitors, which was studied in detail due to its highest content in hydrolyzates, is generated by the hydrolysis of the acetyl group on hemicellulose and is commonly observed along with

the release of xylose. The presence of acetic acid can limited the production of ethanol during fermentation process.

Production of ethanol from lignocellulose has the advantage of abundant and diverse raw material compared to sources such as corn and cane sugars, but requires a great amount of processing to make the sugar monomers available to the microorganisms typically used to produce ethanol by fermentation. Switchgrass and *Miscanthus* are the major value of biomass materials being studied today, due to their high productivity per acre. Cellulose, is contained in nearly every natural, free-growing plant, tree, and bush, in meadows, forests, and fields all over the world without agricultural effort or cost needed to make it grow. One of the benefits of cellulosic ethanol is it reduces greenhouse gas emissions.

Absence of production of cellulosic ethanol in the quantities required by the regulation was the basis of a United States Court of Appeals for the District of Columbia decision announced January 25, 2013 voiding a requirement imposed on car and truck fuel producers in the United States by the Environmental Protection Agency requiring addition of cellulosic biofuels to their products. These issues, along with many other difficult production challenges, lead George Washington University policy researchers to state that "in the short term, [cellulosic] ethanol cannot meet the energy security and environmental goals of a gasoline alternative."

Table 2.1 Properties of xylose, glucose and acetic acid

Component	Xylose	Glucose	Acetic Acid
Molecular formula	C ₅ H ₁₀ O ₅	C ₆ H ₁₂ O ₆	CH ₃ COOH
Molecular Structure			
Molecular Weight (gmol ⁻¹)	150.13	180.156	60.05
Stokes diameter (nm)	0.638	0.726	0.412
Diffusion coefficient (cm ² s ⁻¹)	7.69	6.76	11.9

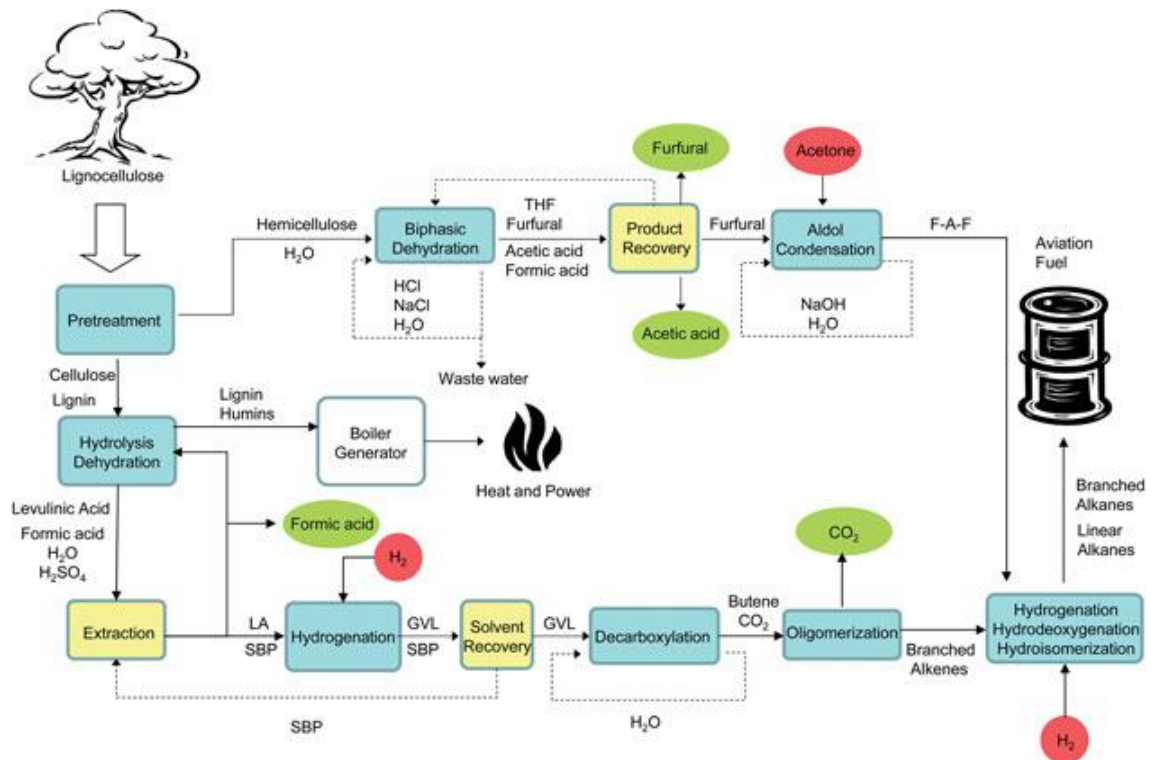


Figure 2.1 Process for biomass.

2.3 Membranes

A membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemical species in a selective manner as shown in Figure 1. The stream that retained by the membrane is the retentate while the one permeates through the membrane is the permeate stream. Either of the two streams retentate or permeate could be the end-use products in a membrane-based separation process (Mulder, 1996). The selectivity of membrane is due to its size, physicochemical interactions, shape, electrostatic charge, diffusivity, volatility and polarity/solubility.

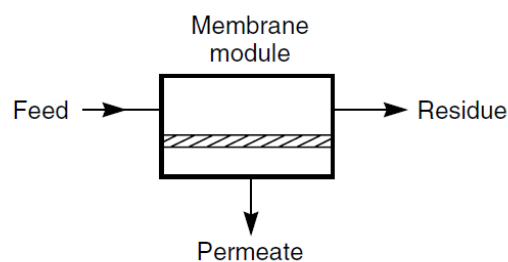


Figure 2.2: Schematic diagram of the basic membrane gas separation process

There are 4 types of membrane module which are plate-and-frame, tubular, spiral wound and hollow fiber. Membrane separation by using hollow fibers has become the one of emerging technologies which underwent a rapid growth during the past few decades. The excellent mass-transfer properties conferred by the hollow fiber configuration led to the numerous commercial applications in various fields such as the medical field (blood fractionation), water reclamation (purification and desalination), ultrafiltration, microfiltration, liquid/liquid or liquid/solid separation, reverse osmosis, gas separation, hemodialysis, removal of VOCs from water and so on (Feng, 2013).

Through this definition, a membrane should always be associated with its application. There are several application of membrane include desolation, dialysis and also filtration to gas separation. Different membrane morphologies will be used depending on the application. In figure 2.2, a schematic representation of different morphologies is given.

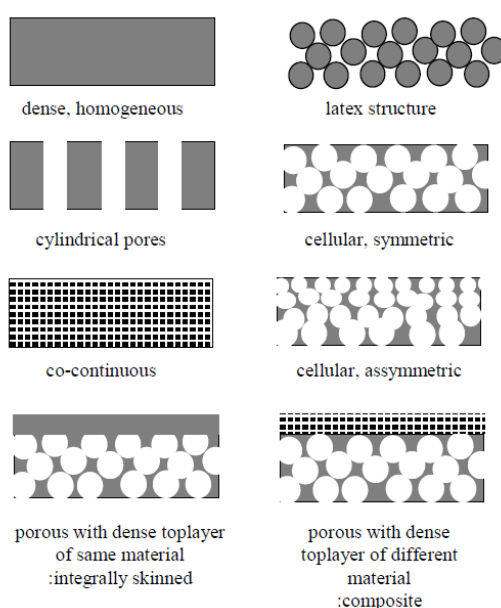


Figure 2.3 Schematic representation of different membrane morphologies; colored parts represent polymer.

There are several types of membrane separation mechanisms exist. In membrane applications, the sorption-diffusion mechanism plays the major role where the choice of the membrane material is based on selective sorption and diffusion properties.

Membrane morphology will not play a major role in issues of selectivity but they do with total flux. For examples of these applications is gas separation, pervaporation and reverse osmosis. The second separation mechanism is based on the size of the species to be separated. Membranes will have typically pore sizes that can give rise to retention of certain species. In table 1.1, the pore sizes of the different membrane categories are given. Besides average pore size and pore size distribution, other parameters like or electrical charge can have a large influence too on its separation characteristics. These membranes are often used in pressure driven processes.

Table 2.2 : Pressure driven processes using porous membranes (J. A. van't et. al, 1992)

Membrane application	Pore size	Typical flux (l/m².h.bar)	Typical Pressure (bar)	Examples of materials retained
Microfiltration	>50nm	>50	0.1-2	Particles (bacteria, yeast)
Ultrafiltration	1nm – 100 nm	10-50	1-5	Macromolecules, colloids
Nanofiltration	≈1 nm	1.4-12	5-20	Solutes Mw > 500, multivalent ions
Reverse Osmosis	Non porous	0.005-1.4	10/100	water

The structure or morphology of the membrane will have an effect on the total flux through the membrane. Decreasing the total thickness of the membranes would therefore be advantageous. However, this is limited due to mechanical stability constraints. This is overcome by preparing asymmetric membranes in which the separating part of the membrane is situated in a thin layer of the membrane. The majority of the structure will only serve as a mechanical support for this selective layer. The selective layer and mechanical support of membranes must be optimized.

	Cut-offs of different liquid filtration techniques							
Micrometer logarithmic scaled	0,001	0,01	0,1	1	10	100	1000	
Angstroms logarithmic scaled	1	10	100	1000	10 ⁴	10 ⁵	10 ⁶	10 ⁷
Molecular weight (Dextran in kD)	0,5	50	7.000					
Size ratio of substances to be separated		Solved salts	Pyrogens	Viruses	Bacteria	Yeast	Pollen	Sand
		Sugar	Albumin (66 kD)		Red blood cells	Human hair		
Atomic radius								
Separating process	Reverse osmosis		Ultra filtration				Particle filtration	
		Nano filtration		Micro filtration				

Figure 2.4: Cut-offs of different liquid filtration techniques.

2.3.1 Membrane Technology

Membrane technology has become a dignified separation technology over the past decennia. The main force of membrane technology is the fact that it works without the addition of chemicals, with a relatively low energy use and easy and well-arranged process conductions. Membrane technology is a generic term for a number of different, very characteristic separation processes. These processes are of the same kind, because in each of them a membrane is used. Membranes are used more and more often for the creation of process water from groundwater, surface water or wastewater. Membranes are now competitive for conventional techniques. The membrane separation process is based on the presence of semi permeable membranes. The principle is quite simple: the membrane acts as a very specific filter that will let water flow through, while it catches suspended solids and other substances. There are various methods to enable substances to penetrate a membrane. Examples of these methods are the applications of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential.

2.4 Membrane Formation

During the three decades of intensive membrane preparation research, different techniques have been proposed to generate selective, permeable films. The most used and thus important class of techniques is called phase inversion techniques. These processes rely on the phase separation of polymer solutions producing porous polymer films. Phase separation mechanisms can generally be subdivided in three main categories depending on the parameters that induce demixing which are temperature induced phase separation (TIPS), reaction induced phase separation (RIPS) and diffusion induced phase separation (DIPS). By posing a change in one of these parameters at one particular side of the film, asymmetric boundaries are posed on the polymer film which can be expressed in the resulting structure. By changing the temperature at the interface of the polymer solution, heat will be exchanged and demixing can be induced (temperature induced phase separation or TIPS). The original polymer solution can also be subjected to a reaction which causes phase separation (reaction induced phase separation) (RIPS). The most used technique is based on diffusion induced phase separation (DIPS). By contacting a polymer solution to a vapour or liquid, diffusional mass exchange will lead to a change in the local composition of the polymer film and demixing can be induced.

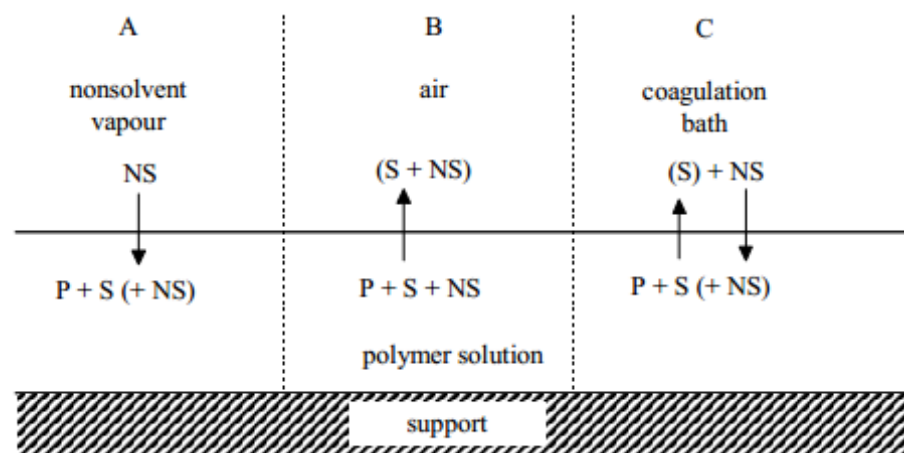


Figure 2.5 Schematic representation of three DIPS processes: A) precipitation with nonsolvent vapor, B) evaporation of solvent, C) immersion precipitation. Main direction of diffusion of the different species is indicated by arrows. Polymer, solvent and nonsolvent are represented with P, S and NS respectively.

Three types of techniques were developed to reach DIPS: coagulation by absorption of nonsolvent from a vapor phase, evaporation of solvent and immersion into a nonsolvent bath. These techniques are schematically represented in figure 2.3. Often combinations of various techniques are made to achieve the desired membrane. When a polymer is subjected to a vapor containing a nonsolvent (a species not miscible with the polymer), often symmetric structures are generated. Membrane formation by evaporation (porous structures) uses polymer solutions containing a volatile solvent, a less volatile nonsolvent and a polymer. Preferential loss of solvent will generate meta- or unstable compositions and phase separation will be induced at this point. Immersion precipitation is achieved by diffusion of nonsolvent from a coagulation bath into the polymer film and diffusion of solvent from the polymer solution into the nonsolvent bath. Although the processes are quite easy to perform, the exact conditions under which a particular membrane will be formed is often derived on empirical grounds.

2.5 Separation Technology For Inhibitor Removal

Acetic acid, one of the inhibitors, which was studied in detail due to its highest content in hydrolyzates, is generated by the hydrolysis of the acetyl group on hemicellulose and is commonly observed along with the release of xylose. The growth of fermentation microorganisms and the production of ethanol are strongly affected by the presence of acetic acid in high concentration. In order to separate acetic acid from hydrolyzates, biological, physical, and chemical methods as well as combined treatments have been employed for example detoxification method including microbiology, vacuum evaporation, extraction, overliming, activated charcoal adsorption, and ion exchange.

2.5.1 Extraction process

Extraction plant consists of the extraction tower, the rectification tower for the recovery of the extraction agent, and the water-stripping tower. As a rule, the feed mixture has a greater density than the solvent, and is fed in at the top end of the

extraction tower. Inside the tower it streams towards the bottom and in the process gives off acetic acid to the extraction agent. Depending on the effort, residual concentrations of 0.1-0.5 wt% can be achieved. Since the aqueous phase is simultaneously saturated with the extraction agent in the extraction tower, it is recovered in a downstream stripping tower. It can in this respect be performed with live steam. The extraction agent accumulates at the top end of the rectification tower and the acetic acid at the bottom of the tower resulting in acetic-acid concentrations of practically 100 wt%. If there is a risk of any higher-boiling components also passing into the organic phase during extraction, then it is recommended that the acetic acid should be discharged in vapor form.

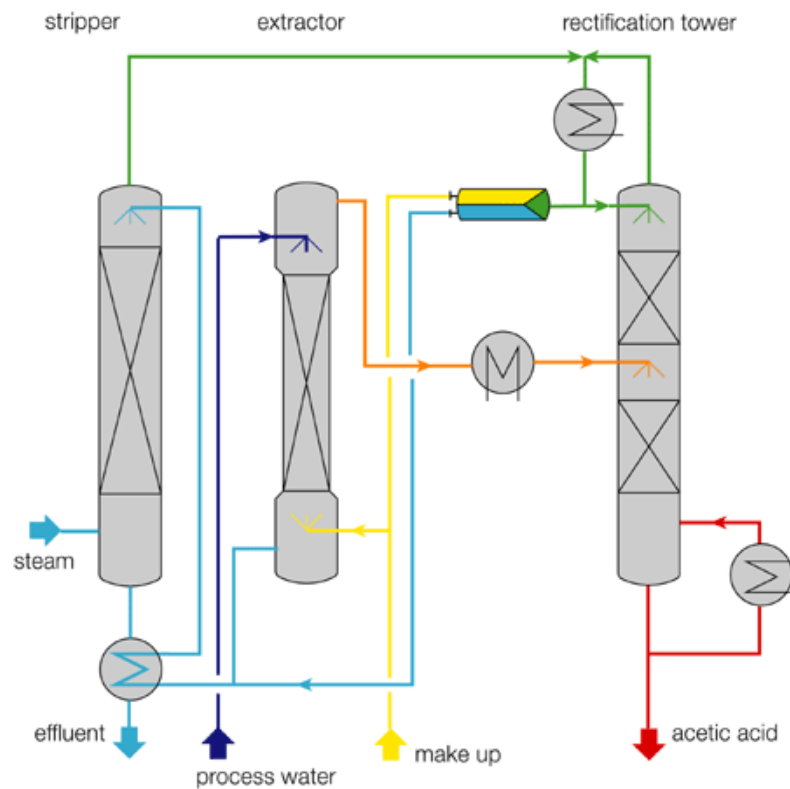


Figure2.6 Flow diagram for extraction process

2.5.1 Evaporation Process

Evaporation is a simple procedure to remove acetic acid, furfural and other volatile components in the hydrolyzates. However, this method retains the concentration of non-volatile toxic compounds (extractives and lignin derivatives) in the hydrolyzates. Palmqvist et al., (1996) observed the removal of most volatile fraction (10% v/v) from willow hemicellulose hydrolyzate by roto-evaporation. Wilson et al., (1989) found a decrease in the concentration of acetic acid, furfural and vanillin by 54%, 100% and 29%, respectively, compared with the concentrations in the hydrolyzate. Larsson et al., (1999) observed the removal of furfural (90%) and HMF (4%) using vacuum evaporation from wood hemicellulosic hydrolyzate. For instance, Converti et al.(2000) hydrolyzed the *E. globules* wood by steam explosion and dilute acid treatment at 100 °C, followed by boiling or evaporating the obtained hydrolyzate for 160 min to decrease the concentration of acetic acid and furfural from 31.2 to 1.0 g/l and from 1.2 to 0.5 g/l, respectively. These are below their inhibitory levels for the fermentation of xylose to xylitol by *Pachysolen tannophilus* strain, showing that in this case the simple evaporation method is sufficient to eliminate the inhibition of acetic acid and furfural. Solvent extraction with ethyl acetate is effective to remove all of the inhibitory compounds except for the residual acetic acid (Wilson et.al,1989) e.g. ethyl acetate extraction can be used to remove 56% acetic acid and all of furfural, vanillin, and 4-hydroxybenzoic acid (Palmqvist, 2000). Solvent extraction with ethyl acetate is effective to remove all of the inhibitory compounds except for the residual acetic acid (Wilson et.al,1989) ,e.g. ethyl acetate extraction can be used to remove 56% acetic acid and all of furfural, vanillin, and 4-hydroxybenzoic acid (Palmqvist, 2000)

Another potential substrate sugarcane bagasse was hydrolyzed and vacuum evaporated followed by activated charcoal treatment, revealed 89% removal of furfural (Rodrigues et al., 2001) with partial elimination of acetic acid. Zhu et al., (2011) applied the complex extraction to detoxify the prehydrolysate corn stover using mixed extractant (30% trialkylamine-50% n-octanol–20% kerosene). The detoxification resulted into removal of 73.3% acetic acid, 45.7% 5-HMF and 100% furfural.

2.5.2 Activated Charcoal Treatment

The detoxification of hemicellulose hydrolysates, by activated charcoal is known to be a cost effective with high capacity to absorb compounds without affecting levels of sugar in hydrolysate (Canilha et al., 2008; Chandel et al., 2007). The effectiveness of activated charcoal treatment depends on different process variables such as pH, contact time, temperature and the ratio of activated charcoal taken versus the liquid hydrolysate volume (Prakasham et al., 2009).

2.5.3 Ion Exchange Resins

Treatment with ion exchange resins has been known to remove lignin-derived inhibitors, acetic acid and furfurals respectively, leading to hydrolysate that show a fermentation similar to that of an inhibitor-free model substrate. The ion-exchange resins based separation of fermentative inhibitors may not be cost effective (Lee et al., 1999), however, it provides most effective means of inhibitor separation when the hydrolyzate being adjusted to a pH of 10 which requires significant quantities of base chemicals (Wilson and Tekere, 2009). Further, the anion treatment also helps to remove most inhibitors (i.e. levulinic, acetic, formic acids, and furfural and 5-HMF).

The effect of four different ion exchange resins (cation and anion) was investigated for the detoxification of *Eucalyptus* hemicellulosic hydrolysates for the improved xylitol production by *Candida guilliermondii* (Villarreal et al., 2006). The ion exchange detoxification drastically enhanced the fermentability of the hydrolyzate. Total 32.7 g/l of xylitol was achieved after 48 h fermentation, which correspond to 0.68 g/l h volumetric productivity and 0.57 g/g xylitol yield factor (Villarreal et al. 2006). The ion exchange resins also led to a considerable loss of fermentable sugars from the hydrolyzate. Chandel et al. (2007) observed that ion exchange resins diminish furans (63.4%) and total phenolics (75.8%) from sugarcane bagasse acid hydrolysates. Although the ion exchanges resins is effective, however is not cost effective that reflects its limited feasibility in commercial industrial purpose in lignocellulosics derived products synthesis.